

Oxidation and Spin State Studies on V-Compounds and Proteins using XMCD and L-Edge Spectroscopy at Beamline 4.02

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INTRODUCTION

XMCD and L-edge spectroscopy give a unique opportunity to study spin and oxidation states of dilute organic and inorganic complexes. Advantages of the technique include element selectivity and high sensitivity. With our current setup we can study dilute systems like metalloproteins with a metal concentration of 500 ppm and below [1]. This gives us the ability to answer widely discussed questions of oxidation and spin states of transition metals in active sites of certain proteins. In this research project we focus on the protein nitrogenase containing Vanadium in the active site. In order to get an overview over the influence of the chemical environment on the L-edge we are performing an extensive study of model compounds, especially V-S-complexes.

EXPERIMENTS

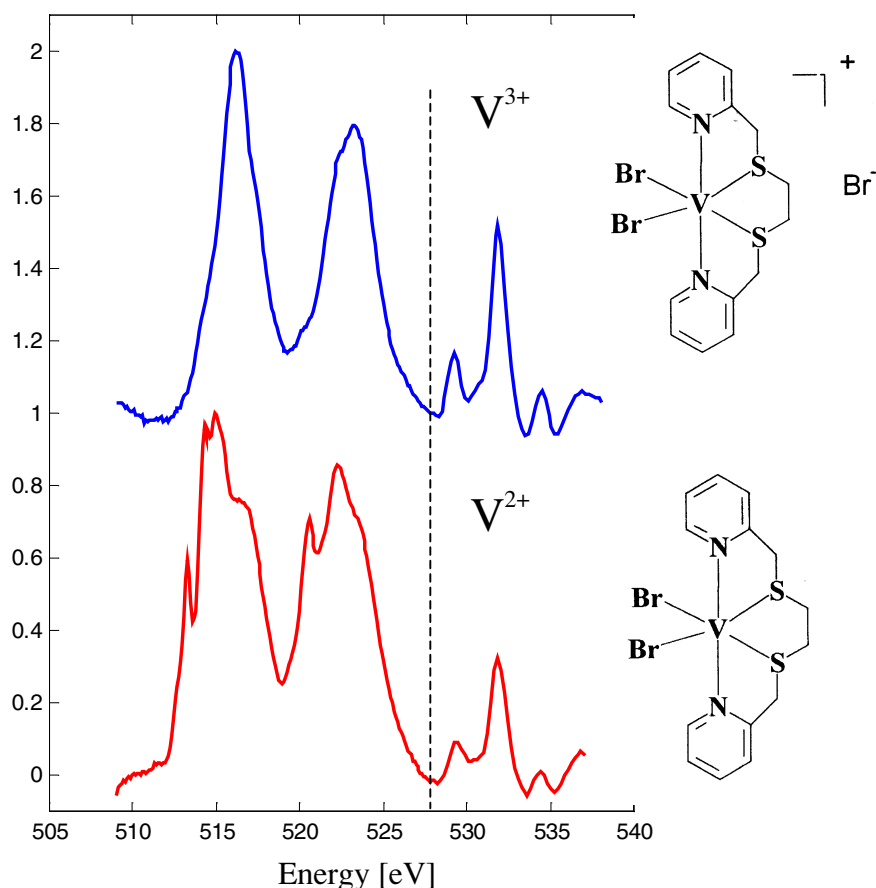
The experiments are done at the elliptical undulator beamline of the ALS. Our current setup allows us to measure the X-ray absorption in fluorescence utilizing a 30 element Ge detector or a high resolution STJ detector developed in collaboration with the low temperature detector group at LLNL [2]. Furthermore, absorption spectra can be taken measuring the photocurrent. This method is favored studying the more concentrated model compounds. To get a relative energy calibration of the L-edge spectra the beam passes a Ti-mesh. The signal of the residual oxygen on the mesh can be used to correct for energy shifts giving a relative energy error on the order of 10 meV.

To perform XMCD-measurements we will bring a 6-Tesla magnet with a pumped He cryostat into operation shortly. This system will be operated at a base temperature of 1 K. Again this will enable us to measure absorption spectra via fluorescence with the 30 element detector array and via photocurrent. The system is equipped with a load lock to do sample loading while the system is cold. With the loading system one also can transfer air sensitive samples in a special designed capped sample holder. This allows to prepare and seal the sample in a glove box and to open the sample holder in the UHV chamber directly before being measured.

Several model compounds have been investigated. The Sulfur ligated Vanadium complexes have been prepared at the University of Hamburg. All samples have been handled in a glove box and ground directly before the measurement. Extensive radiation damage studies showed for some of the complexes a fast degrading in the beam. In general these samples also showed extreme air sensitivity.

INITIAL RESULTS AND OUTLOOK

Two L-edge spectra taken from $V^{2+}Br_2(N_2S_2)$ (S1) and $[V^{3+}Br_2(N_2S_2)]Br$ (S2) are shown in figure 1. In this case a strong dependence on the oxidation state is observed. The S1-spectrum exhibits lots of structure and is shifted in energy with respect to the S2-spectrum which is rather struc-



tureless. In general, a strong dependence of the spectra on the ligands and the oxidation states is observed.

Figure 1. Photocurrent absorption spectra of $V^{2+}Br_2(N_2S_2)$ (red line) and $[V^{3+}Br_2(N_2S_2)]Br$ (blue line). The structure of both compounds is the same, but the oxidation state is different. The figure shows the L_{III} - and L_{II} -lines of Vanadium. The structures above 528 eV (dashed line) are due to absorption in oxygen. The different oxidation states lead to a dramatic change of the L-edge spectra.

In the ongoing study several model compounds have been studied. Calculations of absorption spectra will be performed to get a deeper understanding of the observed spectra. Further measurements using XMCD are planned. The application to dilute V-proteins is on its way.

REFERENCES

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2. Stephan Friedrich et al., Nucl. Inst. Meth., (accepted for 2001)

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